

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C07C 327/36, C08F 2/38, 112/08, 120/14, 120/34, 212/08, 220/14, 220/34, 293/00		A1	(11) International Publication Number: WO 99/05099 (43) International Publication Date: 4 February 1999 (04.02.99)
(21) International Application Number: PCT/AU98/00569 (22) International Filing Date: 20 July 1998 (20.07.98) (30) Priority Data: 60/053,208 21 July 1997 (21.07.97) US (71) Applicants (for all designated States except US): COMMON-WEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANISATION [AU/AU]; Limestone Avenue, Campbell, ACT 2601 (AU). E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): RIZZARDO, Enzo [AU/AU]; 26 Alex Avenue, Wheelers Hill, VIC 3150 (AU). THANG, San, Hoa [AU/AU]; 180 Clarinda Road, Clayton South, VIC 3169 (AU). MOAD, Graeme [AU/AU]; "Bellamy", 137 Monbulk Road, Kallista, VIC 3791 (AU). (74) Agents: CORBETT, Terence, G. et al.; Davies Collison Cave, 1 Little Collins Street, Melbourne, VIC 3000 (AU).			(81) Designated States: AU, BR, CA, IL, JP, KR, MX, NZ, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: SYNTHESIS OF DITHIOESTER CHAIN TRANSFER AGENTS AND USE OF BIS(THIOACYL) DISULFIDES OR DITHIOESTERS AS CHAIN TRANSFER AGENTS (57) Abstract This invention relates to the synthesis of dithiocarboxylic acid esters by reaction of bis(thioacyl) disulphides, thioacetals or vinylidene bis(thioether) with free-radicals (optionally in the presence of monomers). The invention also relates to processes for the synthesis of polymers utilising these dithioesters as polymerisation regulators (chain transfer agents) or to the use of bis(thioacyl) disulphides to generate dithioester chain transfer agents <i>in situ</i> .			

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

SYNTHESIS OF DITHIOESTER CHAIN TRANSFER AGENTS AND USE OF BIS(THIOACYL) DISULFIDES OR DITHIOESTERS AS CHAIN TRANSFER AGENTS

BACKGROUND OF THE INVENTION

5 This invention relates to the synthesis of dithioesters which can be utilized in a free radical polymerization process with characteristics of a living polymerization. The dithioesters may be monomeric, oligomeric or polymeric. The invention also relates to processes for the synthesis of polymers utilising these dithioesters.

10 There is increasing interest in methods for producing a variety of polymers with control of the major variables affecting polymer properties. Living polymerizations provide the maximum degree of control for the synthesis of polymers with predictable well defined structures. The characteristics of a living polymerization are discussed by Quirk and Lee (*Polymer International* 27, 359 (1992)) who give the following experimentally observable criteria:

15

- "1. Polymerization proceeds until all of the monomer has been consumed. Further addition of monomer results in continued polymerization.
2. The number average molecular weight (or the number average degree of polymerization) is a linear function of conversion.
- 20 3. The number of polymer molecules (and active centers) is a constant which is sensibly independent of conversion.
4. The molecular weight can be controlled by the stoichiometry of the reaction.
5. Narrow molecular weight distribution polymers are produced.
- 25 6. Block copolymers can be prepared by sequential monomer addition.
7. Chain end-functionalised polymers can be prepared in quantitative yield."

Thus living polymerization processes can be used to produce polymers of narrow molecular weight distribution containing one or more monomer sequences whose length
30 and composition are controlled by the stoichiometry of the reaction and the degree of conversion. Homopolymers, random copolymers and/or block polymers may be produced

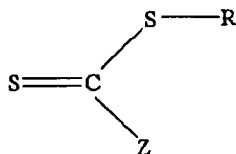
- 2 -

with a high degree of control and with low polydispersity.

Syntheses of certain polymers with xanthate or dithiocarbamate end groups from the corresponding disulfides have been described in the literature (see for example, Moad and Solomon "The Chemistry of Free Radical Polymerization", Pergamon, London, 1995, pp 337-339; Nair and Clouet *J. Macromol. Sci., Rev. Macromol. Chem. Phys.*, **1991**, C31, 311). Processes have also been described that use these compounds to prepare block copolymers. However, the processes using these compounds are unsuccessful in producing low polydispersity polymers and do not meet many of the criteria for living polymerization as defined above.

WO 98/01478, the entire contents of which is incorporated herein by reference, describes the use of chain transfer agents (CTAs) of the following structure:

15



in free radical polymerisation processes with living characteristics to provide polymers of controlled molecular weight and low polydispersity.

It has now been found that CTAs of this structure can be prepared in a convenient manner from a single disulphide reagent, or generated *in situ* in the polymerisation vessel.

25

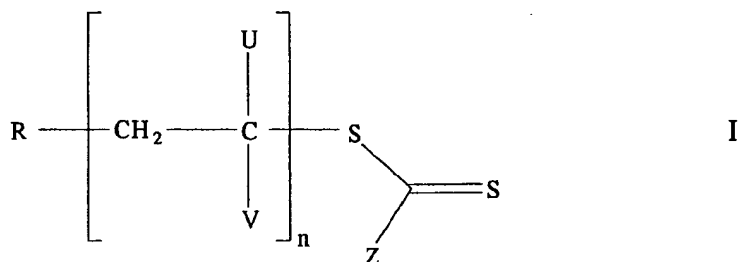
SUMMARY OF THE INVENTION

Accordingly the present invention provides a process for the synthesis of dithioesters formula I:

30

- 3 -

5



where R is derived from a free radical R• and is selected from the group consisting of optionally substituted alkyl; optionally substituted, saturated, unsaturated or aromatic carbocyclic rings; optionally substituted, saturated, unsaturated or aromatic heterocyclic rings; optionally substituted alkylthio, optionally substituted arylthio; optionally substituted alkoxy; optionally substituted dialkylamino; organometallic species; and polymer chains; R• is a free radical leaving group;

15 U is independently selected from the group consisting of hydrogen; halogen; and C₁₋₄ alkyl optionally substituted with one or more substituents independently selected from the group consisting of hydroxy, carboxy, acyloxy, OR'', O₂CR'' and CO₂R'';

V is independently selected from the group consisting of hydrogen, halogen, R'', CO₂H, CO₂R'', COR'', CN, CONH₂, CONHR'', CONR₂'', O₂CR'' and OR'';

Z is selected from the group consisting of hydrogen, chlorine, optionally substituted alkyl, optionally substituted aryl, optionally substituted alkylthio, optionally substituted alkoxycarbonyl,

25 -CO₂R'', -CO₂H, -O₂CR'', -CONR₂'', cyano, -[P(=O)(OR'')₂], and -[P(=O)R'']₂;

R'' is independently selected from the group consisting of optionally substituted C₁₋₁₈ alkyl, optionally substituted C₂₋₁₈ alkenyl, optionally substituted aryl, optionally substituted heterocyclyl, optionally substituted aralkyl, optionally substituted alkaryl,

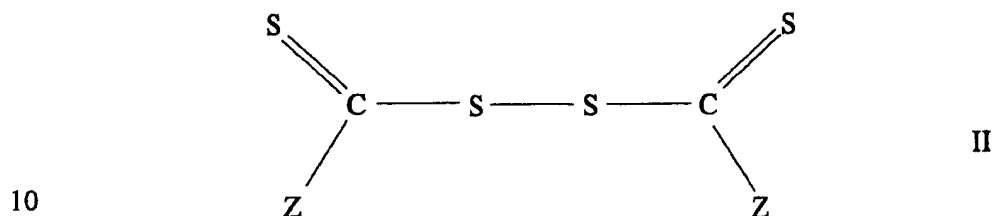
30 wherein said optional substituents are selected from the group consisting of epoxy,

- 4 -

alkoxycarbonyl, aryloxycarbonyl, isocyanato, cyano, silyl, halo and dialkylamino;

and n is 0 or a positive integer,

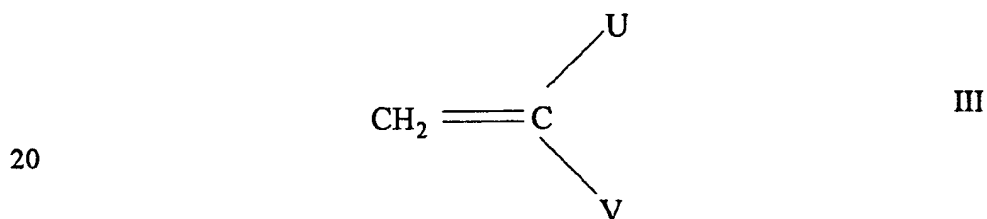
5 which process includes contacting a disulphide of the Formula II:



with

(i) in the case of $n=0$, a free radical of the formula R^\bullet , or

15 (ii) in the case of $n>0$, a free radical of the formula R^\bullet and at least one monomer of the formula III



R may be selected from any organic group which is derived from the corresponding radical, R^\bullet , which radical can act as a free radical leaving group. Preferably the radical, 25 R^\bullet , is capable of initiating free radical polymerisation. Examples of suitable radicals include carbon centred, sulphur centred, and in some circumstances, oxygen or nitrogen centred radicals. Where R is a polymer chain it may be produced by means of free radical polymerisation, or any other means, such as condensation polymerisation.

30 The term "free radical leaving group" as used herein refers to a group which departs as a free radical during a substitution or displacement reaction.

- 5 -

R may also be derived from a dithioester of formula I generated *in situ*, or may be derived from an initiating radical or a propagating radical.

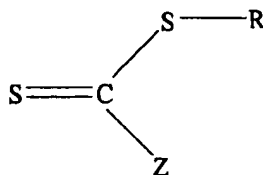
Preferably Z is selected to give the C=S bond a high reactivity towards radical addition while not slowing the subsequent rate of fragmentation in the presence of the monomer to the extent that there is an unacceptable retardation of polymerization.

When conducted in the presence of a monomer of formula III the process according to the invention is useful for the preparation of a wide variety of polymer types, including homopolymers, copolymers and block copolymers. Homopolymers may be prepared by using a single monomer of formula III, while copolymers may be prepared by using two or more monomers. Block copolymers may be prepared by contacting a first monomer of formula III with the disulphide of formula II and free radical of formula R• to produce an intermediate homopolymer of formula I, and then contacting the homopolymer with a second monomer of formula III and a free radical of formula R•. Further blocks can be added in like manner.

The invention also relates to the use of a disulphide of formula II to provide chain transfer in a free radical polymerisation process, and to the use of the disulphide in the preparation of a chain transfer agent of formula I for use in a free radical polymerisation process.

DETAIL OF THE INVENTION

Free radical polymerizations in the presence of chain transfer agents (CTAs) represented by the following structure has been described in Le *et al.* Int. Patent Appl. WO 98/01478.



Such polymerizations possess the characteristics of a living polymerization in that they are

- 6 -

capable of producing polymers of pre-determined molecular weight with narrow molecular weight distribution (low polydispersity), and, by successively adding different monomers, can be used to make block polymers. The process can also be used to produce polymers of more complex architecture, including variously branched homo- and copolymers.

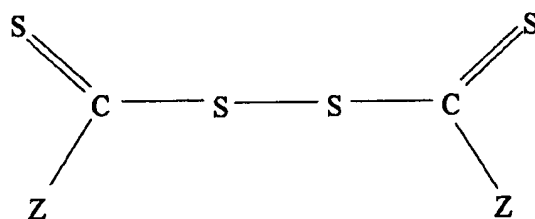
5

It has now been found that certain materials which are not CTAs of the above structure may nonetheless be utilized as precursor materials to said CTAs and with suitable choice of reaction conditions can be used in a 'one-pot' synthesis of CTA and narrow polydispersity polymer.

10

In particular it has now been found that compounds of Formula II react with free radicals produced from a radical source (e.g. an azo compound) to form CTAs of Formula I in moderate to high yields.

15

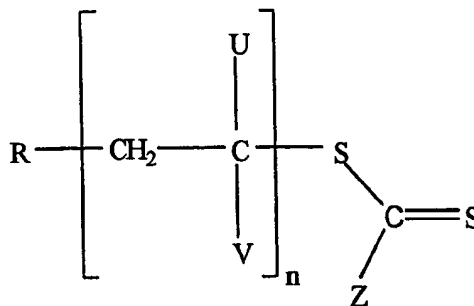


Formula II

20

The reaction may optionally be carried out in the presence of a monomer. The initial product may, in this case, be an oligomeric CTA of Formula I.

25



30

Formula I

- 7 -

When the compound of Formula II is largely consumed polymerization can proceed according to the process disclosed in WO98/01478. It has been found that the overall procedure can be used to synthesise narrow polydispersity and block polymers without the need for product isolation. The process may also be adapted to the synthesis of 5 polymers of more complex architecture through appropriate choice of compound of Formula II and monomers.

The source of free radicals should be chosen such that

- 10 (i) there is a minimum level of initiator derived by-products.
- (ii) the derived group R conveys appropriate reactivity to the product CTA of Formula I.
- 15 (iii) the radical R^\bullet is capable of adding to the desired monomer(s) (so as initiate subsequent polymerization steps).

The requirements for R groups in compounds of Formula I have been described in detail by Le *et al.* Int. Patent Appl. WO 98/01478

20

As used herein the term "dithioester" refers to a compound, which may be monomeric, oligomeric or polymeric having a $-(C=S)S-$ moiety.

Unless specified otherwise the term "alkyl" used either alone or in compound words such 25 as "alkenyloxyalkyl" and "alkylthio" denotes straight chain or branched alkyl, preferably C_{1-20} alkyl. Examples of straight chain and branched alkyl include methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, tert-butyl, amyl, isoamyl, sec-amyl, 1,2-dimethylpropyl, 1,1-dimethylpropyl, hexyl, 4-methylpentyl, 1-methylpentyl, 2-methylpentyl, 3-methylpentyl, 1,1-dimethylbutyl, 2,2-dimethylbutyl, 30 3,3-dimethylbutyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl, 1,2,2-trimethylpropyl, 1,1,2-trimethylpropyl, heptyl, 5-methoxyhexyl, 1-methylhexyl, 2-ethylhexyl, 2,2-

- 8 -

dimethylpentyl, 3,3-dimethylpentyl, 4,4-dimethylpentyl, 1,2-dimethylpentyl, 1,3-dimethylpentyl, 1,4-dimethylpentyl, 1,2,3-trimethylbutyl, 1,1,2-trimethylbutyl, 1,1,3-trimethylbutyl, octyl, 6-methylheptyl, 1-methylheptyl, 1,1,3,3-tetramethylbutyl, nonyl, 1-, 2-, 3-, 4-, 5-, 6- or 7-methyl-octyl, 1-, 2-, 3-, 4- or 5-ethylheptyl, 1-, 2- or 5 3-propylhexyl, decyl, 1-, 2-, 3-, 4-, 5-, 6-, 7- and 8-methylnonyl, 1-, 2-, 3-, 4-, 5- or 6-ethyloctyl, 1-, 2-, 3- or 4-propylheptyl, undecyl, 1-, 2-, 3-, 4-, 5-, 6-, 7-, 8- or 9-methyldecyl, 1-, 2-, 3-, 4-, 5-, 6- or 7-ethylnonyl, 1-, 2-, 3-, 4- or 5-propyloctyl, 1-, 2- or 3-butylheptyl, 1-pentylhexyl, dodecyl, 1-, 2-, 3-, 4-, 5-, 6-, 7-, 8-, 9- or 10-methylundecyl, 1-, 2-, 3-, 4-, 5-, 6-, 7- or 8-ethyldecyl, 1-, 2-, 3-, 4-, 5- or 6- 10 propylnonyl, 1-, 2-, 3- or 4-butyloctyl, 1-2-pentylheptyl and the like.

The term "alkoxy" denotes straight chain or branched alkoxy, preferably C₁₋₂₀ alkoxy. Examples of alkoxy include methoxy, ethoxy, n-propoxy, isopropoxy and the different butoxy isomers.

15

The term "alkenyl" denotes groups formed from straight chain or branched alkenes including ethylenically mono-, di- or poly-unsaturated alkyl groups as previously defined, preferably C₂₋₂₀ alkenyl. Examples of alkenyl include vinyl, allyl, 1-methylvinyl, butenyl, iso-butenyl, 3-methyl-2-butenyl, 1-pentenyl, 1-hexenyl, 3- 20 hexenyl, 1-heptenyl, 3-heptenyl, 1-octenyl, 1-nonenyl, 2-nonenyl, 3-nonenyl, 1-decenyl, 3-decenyl, 1,3-butadienyl, 1,4-pentadienyl, 1,3-hexadienyl and 1,4-hexadienyl

The term "acyl" either alone or in compound words such as "acyloxy", "acylthio", 25 "acylamino" or "diacylamino" denotes carbamoyl, aliphatic acyl group and acyl group containing an aromatic ring, which is referred to as aromatic acyl, or a heterocyclic ring which is referred to as heterocyclic acyl, preferably C₁₋₂₀ acyl. Examples of acyl include carbamoyl; straight chain or branched alkanoyl such as formyl, acetyl, propanoyl, butanoyl, 2-methylpropanoyl, pentanoyl, 2,2-dimethylpropanoyl, hexanoyl, 30 heptanoyl, octanoyl, nonanoyl, decanoyl, undecanoyl, dodecanoyl, tridecanoyl,

- 9 -

tetradecanoyl, pentadecanoyl, hexadecanoyl, heptadecanoyl, octadecanoyl, nonadecanoyl and icosanoyl; alkoxy carbonyl such as methoxycarbonyl, ethoxycarbonyl, t-butoxycarbonyl, t-pentyloxycarbonyl and heptyloxycarbonyl; cycloalkyl carbonyl such as cyclopropyl carbonyl, cyclobutyl carbonyl, 5 cyclopentyl carbonyl and cyclohexyl carbonyl; alkylsulfonyl such as methylsulfonyl and ethylsulfonyl; alkoxy sulfonyl such as methoxy sulfonyl and ethoxy sulfonyl; aroyl such as benzoyl, toluoyl and naphthoyl; aralkanoyl such as phenylalkanoyl (e.g. phenylacetyl, phenylpropanoyl, phenylbutanoyl, phenylisobutyl, phenylpentanoyl and phenylhexanoyl) and naphthylalkanoyl (e.g. naphthylacetyl, naphthylpropanoyl and 10 naphthylbutanoyl); aralkenoyl such as phenylalkenoyl (e.g. phenylpropenoyl, phenylbutenoyl, phenylmethacryloyl, phenylpentenoyl and phenylhexenoyl and naphthylalkenoyl (e.g. naphthylpropenoyl, naphthylbutenoyl and naphthylpentenoyl); aralkoxy carbonyl such as phenylalkoxy carbonyl (e.g. benzyloxy carbonyl); aryloxy carbonyl such as phenoxy carbonyl and naphthoxy carbonyl; aryloxyalkanoyl 15 such as phenoxyacetyl and phenoxypropionyl; aryl carbamoyl such as phenylcarbamoyl; arylthiocarbamoyl such as phenylthiocarbamoyl; arylglyoxyloyl such as phenylglyoxyloyl and naphthylglyoxyloyl; arylsulfonyl such as phenylsulfonyl and naphthylsulfonyl; heterocyclic carbonyl; heterocyclicalkanoyl such as thienylacetyl, thienylpropanoyl, thienylbutanoyl, thienylpentanoyl, thienylhexanoyl, thiazolylacetyl, 20 thiadiazolylacetyl and tetrazolylacetyl; heterocyclicalkenoyl such as heterocyclicpropenoyl, heterocyclicbutenoyl, heterocyclicpentenoyl and heterocyclichexenoyl; and heterocyclicglyoxyloyl such as thiazolylglyoxyloyl and thienylglyoxyloyl.

25 Saturated, unsaturated or aromatic carbocyclic or heterocyclic rings may contain from 3 to 20 carbon atoms.

The terms "aromatic carbocyclic ring" and "aromatic heterocyclic ring" as used herein refer to aromatic and pseudoaromatic rings which may be carbocyclic or heterocyclic, and 30 may be mono or polycyclic ring systems. In the case of heterocyclic rings, there will be one or more heteroatoms selected from N, S, O and P. Examples of suitable rings include

- 10 -

but are not limited to benzene, biphenyl, terphenyl, quaterphenyl, naphthalene, tetrahydronaphthalene, 1-benzyl naphthalene, anthracene, dihydroanthracene, benzanthracene, dibenzanthracene, phenanthracene, perylene, pyridine, 4-phenylpyridine, 3-phenylpyridine, thiophene, benzothiophene, naphthothiophene, thianthrene, furan, 5 pyrene, isobenzofuran, chromene, xanthene, phenoxathiin, pyrrole, imidazole, pyrazole, pyrazine, pyrimidine, pyridazine, indole, indolizine, isoindole, purine, quinoline, isoquinoline, phthalazine, quinoxaline, quinazoline, pteridine, carbazole, carboline, phenanthridine, acridine, phenanthroline, phenazine, isothiazole, isooxazole, phenoxazine and the like, each of which may be optionally substituted. The term "aromatic ring
10 compound(s)" includes molecules, and macromolecules, such as polymers, copolymers and dendrimers which include or consist of one or more aromatic or pseudoaromatic rings. The term "pseudoaromatic" refers to a ring system which is not strictly aromatic, but which is stabilized by means of delocalization of π electrons and behaves in a similar manner to aromatic rings. Examples of pseudoaromatic rings include but are not limited
15 to furan, thiophene, pyrrole and the like.

The terms "saturated carbocyclic ring" and "saturated heterocyclic ring" as used herein refer to carbocyclic and heterocyclic rings, which may be mono or polycyclic ring systems, and which are fully saturated. In the case of heterocyclic rings, there will be one or more
20 heteroatoms selected from N, S, O and P. Examples of suitable rings include, but are not limited to cyclobutane, cyclopentane, cyclohexane, cyclopentane, imidazolidene, pyrazolidene and the like.

The terms "unsaturated carbocyclic ring" and "unsaturated heterocyclic ring" as used
25 herein refer to carbocyclic and heterocyclic rings, which may be mono or polycyclic, which have one or more degrees of unsaturation. In the case of heterocyclic rings, there will be one or more heteroatoms selected from N, S, O and P. Examples of suitable rings include cyclopentene, cyclohexene, imidazoline and pyrazoline.

30 Initiating radicals are free radicals that are derived from the initiator or other species which add monomer to produce propagating radicals. Propagating radicals are radical

- 11 -

species that have added one or more monomer units and are capable of adding further monomer units.

The term "polymer" as used herein includes oligomers and in the case of dithioesters of formula I refers to those in which $n > 1$. The upper limit of a "n" will be defined by the particular conditions and reactants employed, as well as the characteristics of the growing polymer chain.

All of the benefits which derive from the use of radical polymerization can now be realized in synthesis of low polydispersity homo- and copolymers. The ability to synthesize block, graft, star, gradient and end-functional polymers further extends the value of the process as does compatibility with protic monomers and solvents.

The source of initiating radicals can be any suitable method of generating free radicals such as the thermally induced homolytic scission of a suitable compound(s) (thermal initiators such as peroxides, peroxyesters, or azo compounds), the spontaneous generation from monomer (e.g., styrene), redox initiating systems, photochemical initiating systems or high energy radiation such as electron beam, X- or gamma-radiation. The initiating system is chosen such that under the reaction conditions there is no substantial adverse interaction of the initiator or the initiating radicals with the transfer agent under the conditions of the experiment. The initiator should also have the requisite solubility in the reaction medium or monomer mixture.

Suitable sources of free radicals for the process carried out in the absence of monomer are those which generate carbon-centred radicals. These include azo compounds and certain peroxides such as:

2,2'-azobis(isobutyronitrile), 2,2'-azobis(2-cyano-2-butane), dimethyl 2,2'-azobis(methyl isobutyrate), 4,4'-azobis(4-cyanopentanoic acid), 4,4'-azobis(4-cyanopentan-1-ol), 1,1'-azobis(cyclohexanecarbonitrile), 2-(t-butylazo)-2-cyanopropane, 2,2'-azobis[2-methyl-N-(1,1)-bis(hydroxymethyl)-2-hydroxyethyl]

- 12 -

propionamide, 2,2'-azobis[2-methyl-N-hydroxyethyl]-propionamide, 2,2'-azobis(N,N'-dimethyleneisobutyramidine) dihydrochloride, 2,2'-azobis(2-amidinopropane) dihydrochloride, 2,2'-azobis(N,N'-dimethyleneisobutyramine), 2,2'-azobis(2-methyl-N-[1,1-bis(hydroxymethyl)-2-hydroxyethyl] propionamide), 2,2'-
 5 azobis(2-methyl-N-[1,1-bis(hydroxymethyl) ethyl] propionamide), 2,2'-azobis[2-methyl-N-(2-hydroxyethyl) propionamide], 2,2'-azobis(isobutyramide) dihydrate, 2,2'-azobis(2,2,4-trimethylpentane), 2,2'-azobis(2-methylpropane), dilauroyl peroxide, tertiary amyl peroxides and tertiary amyl peroxydicarbonates.

10 For reactions carried out in the presence of monomer where the properties of R• are determined by the nature of the propagating radical formed by addition to monomer a wider range of free radical sources may be used. These include sources of oxygen centred radicals such as the following initiators:

15 t-butyl peroxyacetate, t-butyl peroxybenzoate, t-butyl peroxyoctoate, t-butyl peroxyneodecanoate, t-butylperoxy isobutyrate, t-amyl peroxy pivalate, t-butyl peroxy pivalate, di-isopropyl peroxydicarbonate, dicyclohexyl peroxydicarbonate, dicumyl peroxide, dibenzoyl peroxide, potassium peroxydisulfate, ammonium peroxydisulfate, di-t-butyl hyponitrite, dicumyl hyponitrite.

20

Photochemical initiator systems are chosen to have the requisite solubility in the reaction medium or monomer mixture and have an appropriate quantum yield for radical production under the conditions of the polymerization. Examples include benzoin derivatives, benzophenone, acylphosphine oxides, and photo-redox systems.

25

Redox initiator systems are chosen to have the requisite solubility in the reaction medium or monomer mixture and have an appropriate rate of radical production under the conditions of the polymerization; these initiating systems can include combinations of the following oxidants and reductants:

30

oxidants: potassium peroxydisulfate, hydrogen peroxide, t-butyl hydroperoxide.

- 13 -

reductants: iron (II), titanium (III), potassium thiosulfite, potassium bisulfite.

Other suitable initiating systems are described in recent texts. See, for example, Moad and Solomon "The Chemistry of Free radical Polymerization", Pergamon, London, 1995, pp53-95.

Compounds suitable as monomers or comonomers include the following:

methyl methacrylate, ethyl methacrylate, propyl methacrylate (all isomers), butyl
10 methacrylate (all isomers), 2-ethylhexyl methacrylate, isobornyl methacrylate, methacrylic
acid, benzyl methacrylate, phenyl methacrylate, methacrylonitrile, alpha-methylstyrene,
methyl acrylate, ethyl acrylate, propyl acrylate (all isomers), butyl acrylate (all isomers),
2-ethylhexyl acrylate, isobornyl acrylate, acrylic acid, benzyl acrylate, phenyl acrylate,
acrylonitrile, styrene, functional methacrylates, acrylates and styrenes selected from
15 glycidyl methacrylate, 2-hydroxyethyl methacrylate, hydroxypropyl methacrylate (all
isomers), hydroxybutyl methacrylate (all isomers), N,N-dimethylaminoethyl methacrylate,
N,N-diethylaminoethyl methacrylate, triethyleneglycol methacrylate, itaconic anhydride,
itaconic acid, glycidyl acrylate, 2-hydroxyethyl acrylate, hydroxypropyl acrylate (all
isomers), hydroxybutyl acrylate (all isomers), N,N-dimethylaminoethyl acrylate, N,N-
20 diethylaminoethyl acrylate, triethyleneglycol acrylate, methacrylamide, N-
methylacrylamide, N,N-dimethylacrylamide, N-tert-butylmethacrylamide, N-n-
butylmethacrylamide, N-methylolmethacrylamide, N-ethylolmethacrylamide, N-tert-
butylacrylamide, N-n-butylacrylamide, N-methylolacrylamide, N-ethylolacrylamide, vinyl
benzoic acid (all isomers), diethylaminostyrene (all isomers), alpha-methylvinyl benzoic
25 acid (all isomers), diethylamino alpha-methylstyrene (all isomers), p-vinylbenzene sulfonic
acid, p-vinylbenzene sulfonic sodium salt, trimethoxysilylpropyl methacrylate,
triethoxysilylpropyl methacrylate, tributoxysilylpropyl methacrylate,
dimethoxymethylsilylpropyl methacrylate, diethoxymethyl-silylpropylmethacrylate,
dibutoxymethylsilylpropyl methacrylate, diisopropoxymethylsilylpropyl methacrylate,
30 dimethoxysilylpropyl methacrylate, diethoxysilylpropyl methacrylate, dibutoxysilylpropyl
methacrylate, diisopropoxysilylpropyl methacrylate, trimethoxysilylpropyl acrylate,

- 14 -

triethoxysilylpropyl acrylate, tributoxysilylpropyl acrylate, dimethoxymethylsilylpropyl acrylate, diethoxymethylsilylpropyl acrylate, dibutoxymethylsilylpropyl acrylate, diisopropoxymethylsilylpropyl acrylate, dimethoxysilylpropyl acrylate, diethoxysilylpropyl acrylate, dibutoxysilylpropyl acrylate, diisopropoxysilylpropyl acrylate, vinyl acetate, vinyl butyrate, vinyl benzoate, vinyl chloride, vinyl fluoride, vinyl bromide, maleic anhydride, N-phenylmaleimide, N-butylmaleimide, N-vinylpyrrolidone, N-vinylcarbazole, butadiene, isoprene, chloroprene, ethylene and propylene.

Particularly preferred monomers include styrenic and methacrylate monomers.

10

Unless otherwise specified the term "optionally substituted" as used herein means that the compound, moiety or atom may be substituted with one or more substituents selected from alkyl, alkenyl, alkynyl, aryl, halo, haloalkyl, haloalkenyl, haloalkynyl, haloaryl, hydroxy, alkoxy, alkenyloxy, aryloxy, benzyloxy, haloalkoxy, haloalkenyloxy, haloaryloxy, isocyano, cyano, formyl, carboxyl, dialkylamino, acyl, alkenylacyl, alkynylacyl, arylacyl, acyloxy, alkylsulphonyloxy, arylsulphenyloxy, heterocyclyl, heterocycloxy, haloheterocyclyl, alkylsulphenyl, arylsulphenyl, carboalkoxy, carboaryloxy mercapto, alkylthio, benzylthio, acylthio, sulphonamido, sulfanyl, sulfo and phosphorus-containing groups, alkoxysilyl, silyl, alkylsilyl, alkylalkoxysilyl, phenoxysilyl, alkylphenoxysilyl, alkoxyphenoxy silyl and arylphenoxy silyl.

These substituents do not take part in the polymerization reactions but form part of the terminal groups of the polymer chains and may be capable of subsequent chemical reaction. The low polydispersity polymer containing any such reactive group is thereby able to undergo further chemical transformation, such as being joined with another polymer chain. Suitable reactive substituents include: epoxy, hydroxy, alkoxy, acyl, acyloxy, carboxy (and salts), sulfonic acid (and salts), alkylcarbonyloxy, isocyanato, cyano, silyl, halo, and dialkylamino. Alternatively, the substituents may be non-reactive such as alkoxy, alkyl or aryl. Reactive groups should be chosen such that there is no adverse reaction with the CTA under the conditions of the experiment. For example, groups such as primary or secondary amino under some conditions may react with

- 15 -

dithioesters to give thioamides thus destroying the CTA.

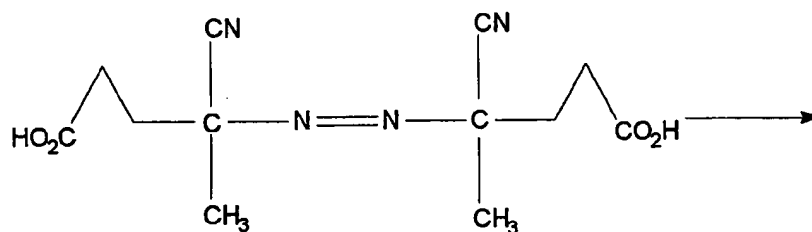
The process of this invention offers a route of compounds of Formula I that may be otherwise difficult to prepare.

5

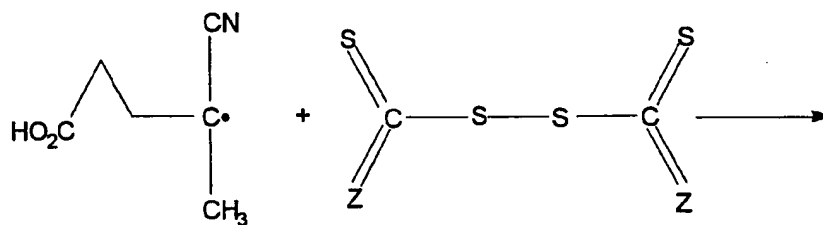
One application is the synthesis of functional dithioesters from an azo compound containing the appropriate functionality as illustrated in the following Scheme.

Scheme 1

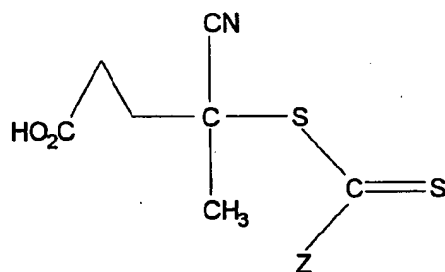
10



15



20



25

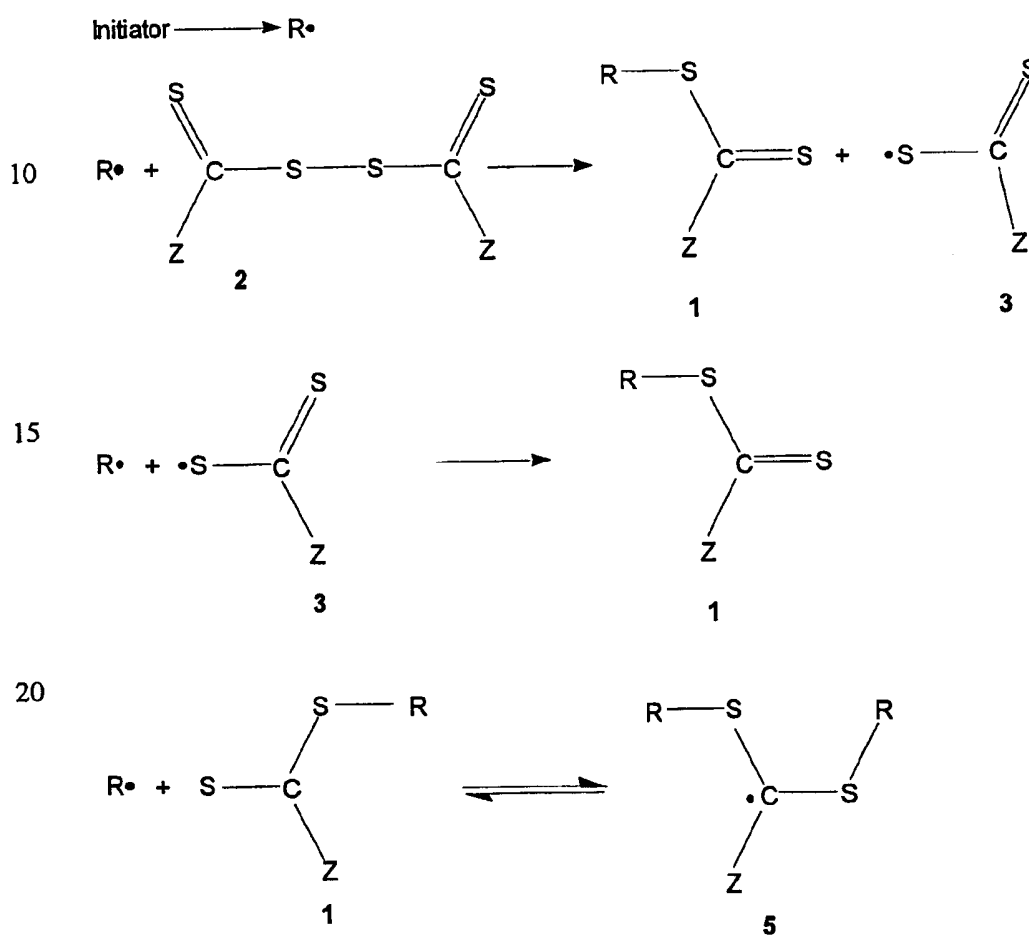
When conducted in the presence of monomers the process also offers a route to narrow polydispersity and block polymers and may be adapted to produce polymers of more complex architecture.

30

Whilst not wishing to be limited to any particular mechanism, it is believed that the mechanism of the process is as summarized in Scheme 2 below. Radicals ($R\cdot$) are formed from a source of free radicals. These react with the compound **2** to form a compound **1** and a thiocarbonylthio radical **3**.

5

Scheme 2



The thiocarbonylthio radical **3** is a poor initiator of polymerization and under the reaction conditions most likely consumed by coupling with another free radical. This radical may be a thiocarbonylthio radical to reform compound **2** or an initiator derived radical ($R\cdot$) to form further compound **1**.

30

The main side reactions occurring under the reaction conditions are most likely the self

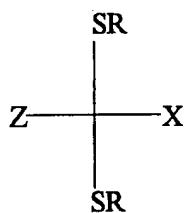
- 17 -

reaction of species $R\cdot$ and other reactions involving the source of free radicals.

For reactions carried out in the presence of a monomer the radical $R\cdot$ may undertake one or more monomer additions before reaction with 1 or 3. In this case the product will be 5 of formula I with $n > 0$.

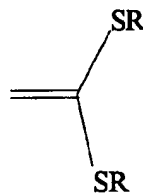
It has also been found that other compounds and processes which generate dithioester compounds of Formula I may be used in similar fashion and thus also form part of this invention. Compounds of this type are represented by formulae V and VI.

10



15

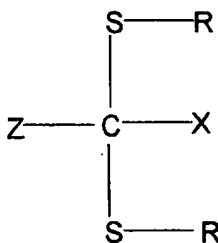
Formula V



Formula VI

Accordingly in another aspect of the present invention there is provided a process for the 20 synthesis of a dithioester of Formula I from a compound of Formula V:

25



Formula V

where Z is as defined above,

30

X is hydrogen, halogen, acyl, aryl or phosphine oxide, and

each R is the same or different and is selected from the group consisting

- 18 -

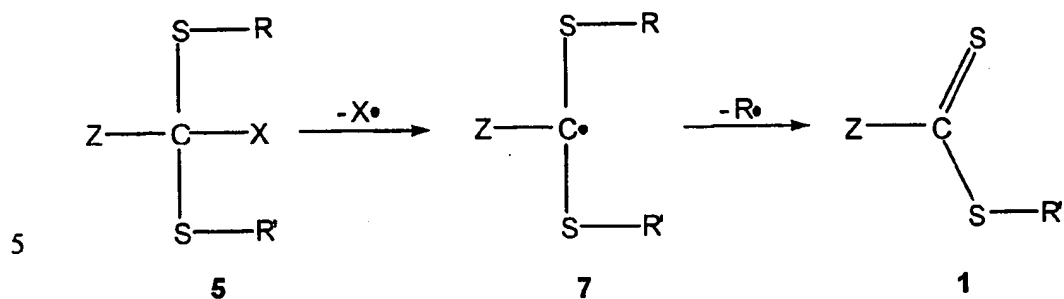
of optionally substituted alkyl; optionally substituted, saturated, unsaturated or aromatic carbocyclic rings; optionally substituted, saturated, unsaturated or aromatic heterocyclic rings; optionally substituted alkylthio, optionally substituted alkylthio; optionally substituted alkoxy; optionally substituted dialkylamino; organometallic species; and polymer chains; and where the corresponding radical, R^\bullet , is a free radical leaving group; by

- A) in the case of $n=0$,
- (i) where X is not hydrogen, homolytic cleavage of the C-X bond of a compound of formula V and subsequent elimination of R^\bullet ,
- (ii) where X is hydrogen, contacting a compound of formula V with a hydrogen abstracting radical followed by elimination of R^\bullet , or
- (iii) contacting a compound of formula V with a Lewis acid followed by elimination of R^\bullet ; or
- B) in the case of $n>0$,
- performing any of (i), (ii) or (iii) in the presence of a monomer of formula III as described above.

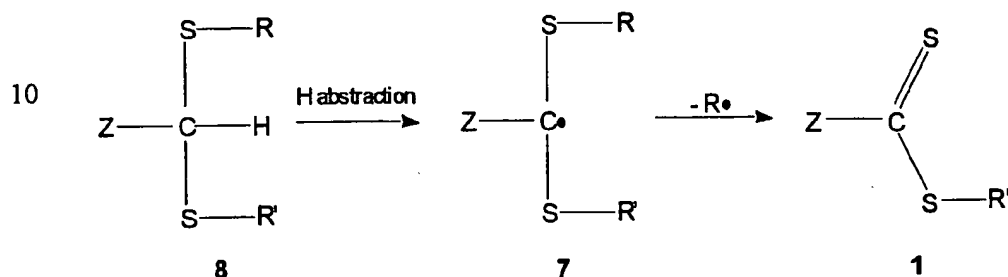
The homolytic cleavage may be achieved by, for example, thermal or photochemical means.

As shown below, homolytic cleavage of the C-X bond of **5** will generate radical **7** which can fragment to give a compound of **1**.

- 19 -



Similarly hydrogen atom abstraction from compound 8 will generate radical 7.

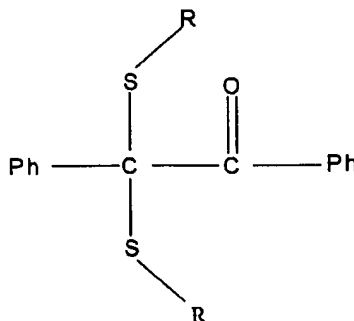


15

Examples of compound of Formula V are thioacetals of benzoin and related species.

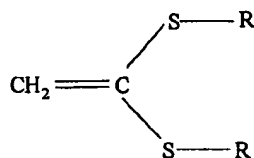
These compounds undergo photochemical homolytic scission.

20



25 In yet another aspect there is provided a process for the synthesis of a dithioester of formula I as defined in claim 1 including contacting a compound of formula VI

30



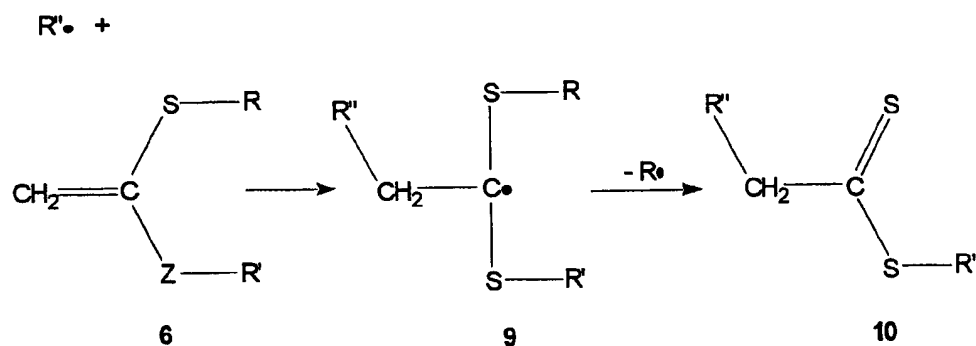
Formula VI

- 20 -

where each R is the same or different and is selected from the group consisting of optionally substituted alkyl; optionally substituted, saturated, unsaturated or aromatic carbocyclic rings; optionally substituted, saturated, unsaturated or aromatic heterocyclic
 5 rings; optionally substituted alkylthio, optionally substituted alkylthio; optionally substituted alkoxy; optionally substituted dialkylamino; organometallic species; and polymer chains; and where the corresponding radical, R^\bullet , is a free radical leaving group;

- with (i) in the case of $n=0$,
 10 a free radical of formula R^\bullet , or
 (ii) in the case of $n>0$,
 a free radical of formula R^\bullet and
 a monomer of Formula III.

- 15 As shown below free radical addition to compound 6 will generate an adduct 9 which can fragment to give a compound 10 (Formula I where $Z = R''CH_2-$)



In these examples both of the groups R and R' must be a free radical leaving groups.

Benefits of the process according to the present invention include the following:

20

- low polydispersity polymers can be synthesised.
- molecular weights increase in a predictable and linear manner with conversion which is controlled by stoichiometry.

- 21 -

- c) the process can be used to provide a variety of low polydispersity polymers.
- d) the process is compatible with a wide range of monomers and reaction conditions.
- 5 e) dithioesters of complex structures may be readily synthesised.

A detailed discussion of the benefits of low polydispersity and the other advantages referred to above is provided in WO 98/01478, including a description of how reactants and conditions can be adjusted to provide desired results.

10

EXAMPLES

General Experimental Conditions

Monomers were purified (to remove inhibitors) and flash distilled immediately prior to
15 use. Degassing was accomplished by repeated freeze-evacuate-thaw cycles. Once degassing was complete ampoules were flame sealed under vacuum and completely submerged in an oil bath at the specified temperature for the specified times. The percentage conversions were calculated gravimetrically.

20 The structures of polymers and block copolymers have been verified by application of appropriate chromatographic and spectroscopic methods. Gel permeation chromatography (GPC) has been used to establish the molecular weight and molecular weight distribution (polydispersity) of the polymers. A Waters Associates liquid chromatograph equipped with differential refractometer and 10^6 , 10^5 , 10^4 , 10^3 , 500 and
25 100 Å Ultrastyrigel columns was used. Tetrahydrofuran (flow rate of 1.0mL/min) was used as eluent. The molecular weights are provided as polystyrene equivalents. The terms M_n , M_w and M_w/M_n are used to indicate the number and weight average molecular weights and the polydispersity respectively.

30 Preparation of Di(thiobenzoyl) Disulfide

The title compound was prepared by oxidizing an aqueous solution of dithiobenzoic acid

- 22 -

sodium salt with a mild oxidizing agent, e.g. an aqueous solution of iodine.

An aqueous solution of iodine (1.0 N, 100 mL) was added dropwise to a stirred aqueous solution of dithiobenzoic acid sodium salt (0.1 mol in 100 mL of water) at room temperature over 15 minutes. Diethyl ether (100 mL) was added, the organic layer separated and washed twice with water, dried (Na_2SO_4), filtered and concentrated *in vacuo*. Di(thiobenzoyl) disulfide (7.5 g, 50%) was obtained after recrystallization from hot ethanol, m.p. 89-91 °C [lit (Houben, *Chem. Ber.*, 39, 3219-3233, (1906). m.p. 92.5 °C]. $^1\text{H-nmr}$ (CDCl_3) δ (ppm) 7.44 (m, 4H, meta-ArH); 7.62 (m, 2H, para-ArH) and 8.11 (m, 4H, ortho-ArH).

Examples 1 and 4-6 demonstrate the synthesis of a low molecular weight dithio-compound by generating free radicals in the presence of di(thiobenzoyl) disulfide.

15

EXAMPLE 1

Preparation of 4-Cyano-4-(thiobenzoylthio)pentanoic Acid

20 A solution of ethyl acetate (10 mL) containing 4,4'-azobis(4-cyanopentanoic acid) (500 mg) and thiobenzoyl disulfide (612 mg) was placed in a reaction vessel which was degassed by three freeze-evacuate-thaw cycles, sealed under vacuum, and heated at 70°C for 24 hours. After removal of the volatiles *in vacuo*, the crude product was subjected to column chromatography (40 g Kieselgel-60, 70-230 mesh) with ethyl acetate : n-hexane 25 : acetonitrile 4 : 5 : 1 as eluent, the title compound was obtained as a red oil, 0.51 g (51.2 % yield). The product solidified on standing in a freezer at -20°C, m.p. 97-99 °C. $^1\text{H-nmr}$ (CDCl_3) δ (ppm) 1.95 (s, 3H, CH_3); 2.40-2.80 (m, 4H, CH_2CH_2); 7.42 (m, 2H, meta-ArH); 7.60 (m, 1H, para-ArH) and 7.91 (m, 2H, ortho-ArH).

30 The following two examples demonstrate the 'one-pot' synthesis of oligomeric dithio compound and narrow polydispersity polymer by conducting a polymerization in the

- 23 -

presence of di(thiobenzoyl) disulfide.

EXAMPLE 2

5 Preparation of low polydispersity PMMA by free radical initiated polymerization of methyl methacrylate in the presence of di(thiobenzoyl) disulfide

A stock solution containing methyl methacrylate (15 mL), azobisisobutyronitrile (20 mg) in benzene (5 mL) was prepared. Aliquots (4 mL) were transferred to ampoules
10 containing di(thiobenzoyl) disulfide (13.8 mg) which were degassed, sealed and heated at 60 °C for the times indicated in the Table. Results are summarized below.

Table 1: GPC molecular weight data of PMMA prepared via solution polymerization with thiobenzoyl disulfide at 60 °C.

15	Entry	Time/hr	Mn ^a	Mw/Mn	% Conv.
	1	16	256	1.24	0.7
	2	115.5	39666	1.10	50.4

(a) GPC molecular weight in polystyrene standard equivalents.

20

EXAMPLE 3

Preparation of low polydispersity polystyrene by thermal polymerization of styrene in the presence of di(thiobenzoyl) disulfide

25

A stock solution of freshly distilled styrene (5 mL) and di(thiobenzoyl) disulfide (45 mg, 1.47×10^{-4} mol) was prepared. Aliquots (2 mL) of this solution were transferred to ampoules (for entries 2 and 3) and freshly distilled styrene (2 mL) transferred to an ampoule labelled control run (entry 1) which were degassed, sealed and heated at 110 °C
30 for the times indicated in the Table below. The polymerization gave narrow polydispersity polystyrene (PD 1.07) (Table 2, entry 3).

- 24 -

Table 2: GPC molecular weight data for the thermal polymerization of styrene with thiobenzoyl disulfide at 100°C

Entry	Time/hr	Mn ^a	Mw/Mn	% Conv.
1 (control)	3	319638	1.62	14.8
2	3	360	1.45	2.7
3	16	8197	1.07	30.7

EXAMPLE 4

Preparation of 4-Cyano-1-hydroxypent-4-yl dithiobenzoate

The 4-cyano-1-hydroxypent-4-yl dithiobenzoate was prepared by heating a degassed solution of 4,4'-azobis(4-cyano-*n*-pentanol) and di(thiobenzoyl) disulfide at 70°C in ethyl acetate for 24 hours. The desired product was isolated in 46% yield.

Procedure:

A solution of di(thiobenzoyl) disulfide (0.73 g, 2.4 mmol) and 4,4'-azobis(4-cyano-*n*-pentanol) (0.50 g, 2 mmol) in ethyl acetate (10 mL) was prepared. The mixture was degassed and heated to 70°C in a Young's vessel for 24 hours. The volatiles were removed under reduced pressure and the residue chromatographed using a mixture of ethyl acetate/petroleum spirits/acetonitrile (6:14:1) as eluant to isolate the title compound (0.49 g, 1.85 mmol, 46%). ¹H-nmr (CDCl₃) δ (ppm) 1.90(3H, CH₃), 2.10(2H, CH₂), 2.30(2H, CH₂), 3.75(2H, CH₂), 7.40, 7.50, 7.90 (5H, ArH).

The following Examples (5-7) demonstrate the use of dithioesters prepared by way of bis(thiobenzoyl) disulfide in the synthesis of narrow polydispersity polymers

- 25 -

EXAMPLE 5**Preparation of 2-cyanobut-2-yl dithiobenzoate**

5 The 2-cyanobut-2-yl dithiobenzoate was prepared by heating a degassed solution of 2,2'-azobis(2-cyano-2-butane) and di(thiobenzoyl) disulfide at 70°C in ethyl acetate for 24 hours. The desired product was isolated in 82% yield.

Procedure:

10 A solution of di(thiobenzoyl) disulfide (0.4g, 1.3 mmol) and 2,2'-azobis(2-cyano-2-butane) (0.53g, 2.76 mmol) in ethyl acetate (5 mL) was prepared. The mixture was degassed and heated at 70°C in a Young's vessel for 24 hours. The volatiles were removed under reduced pressure and the residue chromatographed on a silica-gel column using a mixture of ethyl acetate/n-hexane (1:9) as eluent to isolate the title compound (0.25 g, 82%). ¹H-
15 nmr (CDCl₃) δ (ppm) 1.23 (t, 3H), 1.92 (s, 3H), 2.10 (dt, 1H), 2.30 (dt, 1H), 7.40 (m, 2H, meta-ArH), 7.57 (m, 1H, para-ArH) and 7.91 (m, 2H, ortho-ArH).

EXAMPLE 6

20

Preparation of 1-cyano-1-cyclohexyl dithiobenzoate

Similarly, as in Example 5, the 1-cyano-1-cyclohexyl dithiobenzoate was prepared by heating a degassed solution of 1,1'-azobis(cyclohexanecarbonitrile) and di(thiobenzoyl) disulfide at 70°C in ethyl acetate for 48 hours.

25

Procedure:

A solution of di(thiobenzoyl) disulfide (0.4g, 1.3 mmol) and 1,1'-azobis(cyclohexanecarbonitrile) (0.67g, 2.74 mmol) in ethyl acetate (5.0 mL) was prepared. The mixture was degassed and heated at 70°C in a Young's vessel for 48 hours.

30 The volatiles were removed under reduced pressure and the residue chromatographed on a silica-gel column using a mixture of ethyl acetate/petroleum spirits 40-60°C (1:9) as

- 26 -

eluent to isolate the title compound.

EXAMPLE 7

5 Preparation of low polydispersity polystyrene in the presence of hydroxy-terminated dithioester, 4-cyano-1-hydroxypent-4-yl dithiobenzoate

A solution of hydroxy-terminated dithioester such as 4-cyano-1-hydroxypent-4-yl dithiobenzoate (31.3mg) in styrene (2mL) was prepared and transferred to an ampoule.
 10 The contents were degassed and heated at 100°C for 16hrs. The volatiles were removed and the residue dried to constant weight and analysed by GPC (see Table 3).

Table 3: GPC molecular weight data of polymerisation of styrene with 4-cyano-1-hydroxypent-4-yl dithiobenzoate at 100°C.

15	Dithioester	Time/hr	Mn ^a	Mw/Mn	% Conv.
	Hydroxy dithio	16	2808	1.04	17.0

a) GPC molecular weight in polystyrene standard equivalents.

The end groups in polystyrene, prepared in the presence of the hydroxy-terminated
 20 dithioester were confirmed by the ¹H-nmr spectroscopy. The signals at δ 3.4-3.5 ppm were assigned to the CH₂OH protons and those at δ 7.9 ppm to the ortho-phenyl protons of the terminal thiobenzoylthio group.

EXAMPLE 8

25

Preparation of low polydispersity poly(methyl methacrylate) in the presence of hydroxy-terminated dithioester, 4-cyano-1-hydroxypent-4-yl dithiobenzoate

A stock solution of MMA (7.5mL), benzene (2.5mL) and AIBN (10mg) was prepared and
 30 labelled Solution (I). A 2mL aliquot of solution (I) was used as the control, labelled A. An aliquot of solution (I) (4 mL) was used to dissolve 12mg of 4-cyano-1-hydroxypent-

- 27 -

4-yl dithiobenzoate, divided into two portions and labelled B and C. The samples were degassed, the ampoules sealed under vacuum and heated at 60°C for period of times indicated in Table 4. The volatiles in each sample were removed, the residue dried to constant weight and the products analysed by GPC. The results are summarized in Table.

5

Table 4: GPC molecular weight data of polymerization of MMA with 4-cyano-1-hydroxypentyl dithiobenzoate using AIBN as initiator at 60°C.

10	Entry	Time/hr	Mn ^a	Mw/Mn	% Conv.
	1 (control)	3	310 080	1.64	76.0
	2	3	11 200	1.14	17.0
	3	16	55 300	1.05	92.0

a) GPC molecular weight in polystyrene standard equivalents.

15

EXAMPLE 9

**Preparation of low polydispersity poly(N,N-dimethylaminoethyl methacrylate)
in the presence of carboxy-terminated dithioester,
4-cyano-4-(thiobenzoylthio)pentanoic acid**

20

A stock solution comprising of N,N-dimethylaminoethyl methacrylate monomer (DMAEMA) (7.5 mL), 4,4'-azobis(4-cyanopentanoic acid) (8.5 mg) and 4-cyano-4-(thiobenzoylthio)pentanoic acid (35.0 mg) in ethyl acetate (10 mL) was prepared. Aliquots of the stock solution (4 mL) were transferred to three ampoules which were
25 degassed, sealed, and heated at 60°C for the specified times listed in Table. The polymerizations show excellent control in molecular weight and polydispersity (1.1-1.3).

30

- 28 -

Table 5: Molecular weight data of poly(DMAEMA) using Carboxy-terminated dithioester, 4-cyano-4-(thiobenzoylthio)pentanoic acid at 60°C.

Entry	Time/hr	Mn ^a	Mw/Mn	% Conv.
1	4	3316	1.31	9.0
2	8	11257	1.12	28.3
3	16	21559	1.13	61.8

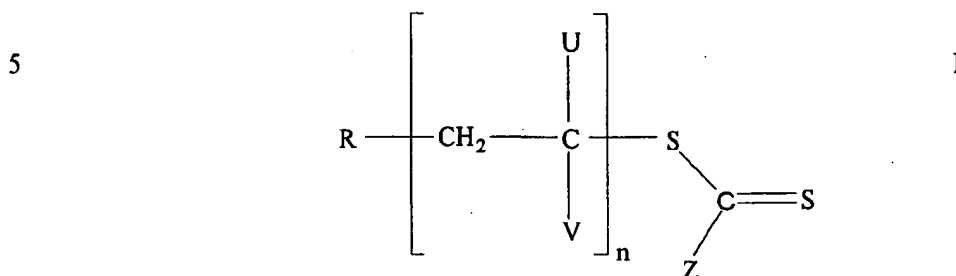
a) GPC molecular weight in polystyrene equivalents.

10 Throughout this specification and the claims which follow, unless the context requires otherwise, the word "comprise", and variations such as "comprises" and "comprising", will be understood to imply the inclusion of a stated integer or step or group of integers or steps but not the exclusion of any other integer or step or group of integers or steps.

15 Those skilled in the art will appreciate that the invention described herein is susceptible to variations and modifications other than those specifically described. It is to be understood that the invention includes all such variations and modifications. The invention also includes all of the steps, features, compositions and compounds referred to or indicated in this specification, individually or collectively, and any and all
20 combinations of any two or more of said steps or features.

CLAIMS:

1. A process for the synthesis of a dithioester of formula I:



- 10 where R is derived from a free radical R• and is selected from the group consisting of optionally substituted alkyl; optionally substituted, saturated, unsaturated or aromatic carbocyclic rings; optionally substituted, saturated, unsaturated or aromatic heterocyclic rings; optionally substituted alkylthio, optionally substituted alkylthio; optionally substituted alkoxy; optionally substituted dialkylamino; organometallic species; and polymer chains; R•
15 is a free radical leaving group;

U is independently selected from the group consisting of hydrogen; halogen; and C₁₋₄ alkyl optionally substituted with one or more substituents independently selected from the group consisting of hydroxy, carboxy, acyloxy, OR'', O₂CR'' and CO₂R'';

20

V is independently selected from the group consisting of hydrogen, halogen, R'', CO₂H, CO₂R'', COR'', CN, CONH₂, CONHR'', CONR₂'', O₂CR'' and OR'';

- Z is selected from the group consisting of hydrogen, chlorine, optionally substituted alkyl,
25 optionally substituted aryl, optionally substituted alkylthio, optionally substituted alkoxy carbonyl, -CO₂R'', -CO₂H, -O₂CR'', -CONR₂'', cyano, [-P(=O)(OR'')₂], and [-P(=O)R'']₂;

- R'' is independently selected from the group consisting of optionally substituted C₁₋₁₈ alkyl,
30 optionally substituted C₂₋₁₈ alkenyl, optionally substituted aryl, optionally substituted heterocyclyl, optionally substituted aralkyl, optionally substituted alkaryl, wherein said

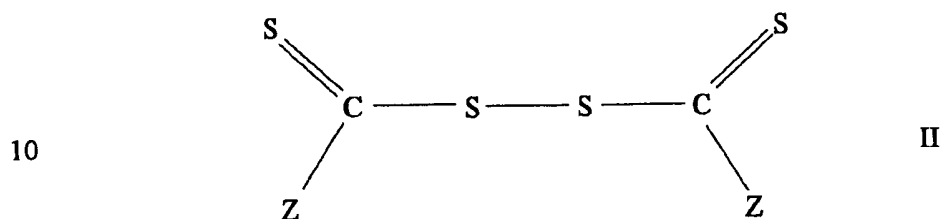
- 30 -

acyl, acyloxy, carboxy (and salts), sulphonic acid (and salts), alkoxycarbonyl, aryloxycarbonyl, isocyanato, cyano, silyl, halo and dialkylamino;

and n is 0 or a positive integer,

5

which process includes contacting a disulphide of the Formula II:

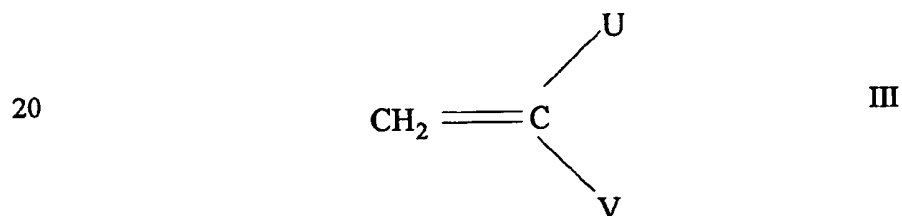


with

(i) in the case of $n=0$, a free radical of the formula R^\bullet , or

15

(ii) in the case of $n>0$, a free radical of the formula R^\bullet and at least one monomer of the formula III



2. A process for the synthesis of a dithioester of Formula I as defined in claim 1 from a compound of formula V

25



Formula V

- 31 -

where Z is as defined above,

X is hydrogen, halogen, acyl, aryl or phosphine oxide, and

each R is the same or different and is selected from the group consisting
of optionally substituted alkyl; optionally substituted, saturated,
unsaturated or aromatic carbocyclic rings; optionally substituted,
saturated, unsaturated or aromatic heterocyclic rings; optionally
substituted alkylthio, optionally substituted alkylthio; optionally
substituted alkoxy; optionally substituted dialkylamino; organometallic
species; and polymer chains; and where the corresponding radical, R^\bullet , is
a free radical leaving group; by

A) in the case of $n=0$,

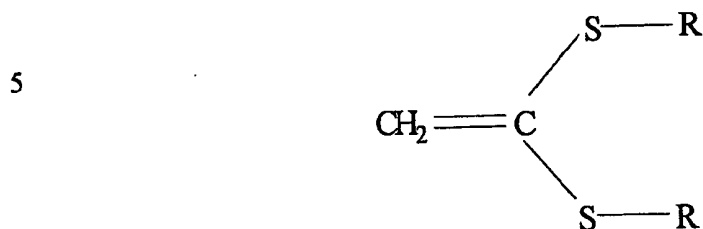
- (i) where X is not hydrogen, homolytic cleavage of the C-X bond of a compound of formula V and subsequent elimination of R^\bullet ,
- (ii) where X is hydrogen, contacting a compound of formula V with a hydrogen abstracting radical followed by elimination of R^\bullet , or
- (iii) contacting a compound of formula V with a Lewis acid followed by elimination of R^\bullet ; or

B) in the case of $n>0$,

performing any of (i), (ii) or (iii) in the presence of a monomer of formula III as defined in claim 1.

- 32 -

3. A process for the synthesis of a composition of matter of Formula I as defined in claim 1 including contacting a compound of formula VI



10 Formula VI

where each R is the same or different and is selected from the group consisting of optionally substituted alkyl; optionally substituted, saturated, unsaturated or aromatic carbocyclic rings; optionally substituted, saturated, unsaturated or aromatic heterocyclic rings; optionally substituted alkylthio, optionally substituted alkylthio; optionally substituted alkoxy; optionally substituted dialkylamino; organometallic species; and polymer chains; and where the corresponding radical, R•, is a free radical leaving group;

- 20 with (i) in the case of $n=0$,
a free radical of formula R•, or
(ii) in the case of $n>0$,
a free radical of formula R• and
a monomer of Formula III.

25

4. A process according to any one of claims 1 to 3 wherein R• is capable of initiating free radical polymerisation.
5. A process according to any one of claims 1 to 3 wherein R is a polymer chain.
- 30 6. A process according to claim 5 wherein the polymer chain is produced by means

- 33 -

of free radical polymerisation.

7. A process according to claim 5 wherein the polymer chain includes or consists of a polymer produced by non-free radical means.
- 5 8. A process according to claim 7 wherein the polymer produced by non-free radical means is a condensation polymer.
9. A process according to claim 1 wherein R is derived from a dithioester of Formula I generated *in situ*.
- 10 10. A process according to any one of claims 1 to 3 wherein R is derived from an initiating radical.
- 15 11. A process according to any one of claims 1 to 3 wherein R is derived from a propagating radical.
12. A process according to any one of claims 1 to 3 wherein the monomer of Formula III is selected from:
- 20 methyl methacrylate, ethyl methacrylate, propyl methacrylate (all isomers), butyl methacrylate (all isomers), 2-ethylhexyl methacrylate, isobornyl methacrylate, methacrylic acid, benzyl methacrylate, phenyl methacrylate, methacrylonitrile, alpha-methylstyrene, methyl acrylate, ethyl acrylate, propyl acrylate (all isomers),
- 25 butyl acrylate (all isomers), 2-ethylhexyl acrylate, isobornyl acrylate, acrylic acid, benzyl acrylate, phenyl acrylate, acrylonitrile, styrene, functional methacrylates, acrylates and styrenes selected from glycidyl methacrylate, 2-hydroxyethyl methacrylate, hydroxypropyl methacrylate (all isomers), hydroxybutyl methacrylate (all isomers), N,N-dimethylaminoethyl methacrylate, N,N-diethylaminoethyl methacrylate, triethyleneglycol methacrylate, itaconic
- 30 anhydride, itaconic acid, glycidyl acrylate, 2-hydroxyethyl acrylate, hydroxypropyl

- 34 -

- acrylate (all isomers), hydroxybutyl acrylate (all isomers), N,N-dimethylaminoethyl acrylate, N,N-diethylaminoethyl acrylate, triethyleneglycol acrylate, methacrylamide, N-methylacrylamide, N,N-dimethylacrylamide, N-tert-butylmethacrylamide, N-n-butylmethacrylamide, N-methylolmethacrylamide, N-ethylolmethacrylamide, N-tert-butylacrylamide, N-n-butylacrylamide, N-methylolacrylamide, N-ethylolacrylamide, vinyl benzoic acid (all isomers), diethylaminostyrene (all isomers), alpha-methylvinyl benzoic acid (all isomers), diethylamino alpha-methylstyrene (all isomers) p-vinylbenzene sulfonic acid, p-vinylbenzene sulfonic sodium salt, trimethoxysilylpropyl methacrylate, triethoxysilylpropyl methacrylate, tributoxysilylpropyl methacrylate, dimethoxymethylsilylpropyl methacrylate, diethoxymethylsilylpropyl methacrylate, dibutoxymethylsilylpropyl methacrylate, diisopropoxymethylsilylpropyl methacrylate, dimethoxysilylpropyl methacrylate, diethoxysilylpropyl methacrylate, dibutoxysilylpropyl methacrylate, diisopropoxysilylpropyl methacrylate, trimethoxysilylpropyl acrylate, triethoxysilylpropyl acrylate, tributoxysilylpropyl acrylate, dimethoxymethylsilylpropyl acrylate, diethoxymethylsilylpropyl acrylate, dibutoxymethylsilylpropyl acrylate, diisopropoxymethylsilylpropyl acrylate, dimethoxysilylpropyl acrylate, diethoxysilylpropyl acrylate, dibutoxysilylpropyl acrylate, diisopropoxysilylpropyl acrylate, vinyl acetate, vinyl butyrate, vinyl benzoate, vinyl chloride, vinyl fluoride, vinyl bromide, maleic anhydride, N-phenylmaleimide, N-butylmaleimide, N-vinylpyrrolidone, N-vinylcarbazole, butadiene, isoprene, chloroprene, ethylene and propylene.
13. A process according to claim 12 wherein the monomer is selected from styrenic monomers and methacrylate monomers.
14. A process according to claim 2 wherein Z is a group capable of activating the C=S bond of the dithioester of Formula I towards radical addition, while not substantially slowing the rate of fragmentation.
15. A process according to claim 3 where the group RCH_2 is selected from a group

- 35 -

capable of activating the C=S bond of the dithioester of Formula I towards radical addition, while not substantially slowing the rate of fragmentation.

16. A process according to claim 10 wherein the initiating radical is derived from a
5 compound selected from the group consisting of:

2,2'-azobis(isobutyronitrile), 2,2'-azobis(2-cyano-2-butane), dimethyl 2,2'-
azobis(methyl isobutyrate), 4,4'-azobis(4-cyanopentanoic acid), 4,4'-azobis(4-
cyanopentan-1-ol), 1,1'-azobis(cyclohexanecarbonitrile), 2-(t-butylazo)-2-
10 cyanopropane, 2,2'-azobis[2-methyl-N-(1,1)-bis(hydroxymethyl)-2-hydroxyethyl]
propionamide, 2,2'-azobis[2-methyl-N-hydroxyethyl]-propionamide, 2,2'-
azobis(N,N'-dimethyleneisobutyramidine) dihydrochloride, 2,2'-azobis(2-
amidinopropane) dihydrochloride, 2,2'-azobis(N,N'-dimethyleneisobutyramine),
2,2'-azobis(2-methyl-N-[1,1-bis(hydroxymethyl)-2-hydroxyethyl] propionamide),
15 2,2'-azobis(2-methyl-N-[1,1-bis(hydroxymethyl) ethyl] propionamide), 2,2'-
azobis[2-methyl-N-(2-hydroxyethyl) propionamide], 2,2'-azobis(isobutyramide)
dihydrate, 2,2'-azobis(2,2,4-trimethylpentane) and 2,2'-azobis(2-methylpropane),
dilauroyl peroxide, tertiary amyl peroxides and tertiary amyl peroxydicarbonates.

- 20 17. A process according to claim 11 wherein the propagating radical is formed by
addition of an initiator to the monomer.

18. A process according to claim 17 wherein the initiator is selected from:

25 t-butyl peroxyacetate, t-butyl peroxybenzoate, t-butyl peroxyoctoate, t-butyl
peroxyneodecanoate, t-butylperoxy isobutyrate, t-amyl peroxy pivalate, t-butyl
peroxy pivalate, di-isopropyl peroxydicarbonate, dicyclohexyl peroxydicarbonate,
dicumyl peroxide, dibenzoyl peroxide, potassium peroxydisulfate, ammonium
peroxydisulfate, di-t-butyl hyponitrite and dicumyl hyponitrite.

30

19. A process for preparing a homopolymer of Formula I as claimed in claim 1

- 36 -

wherein a single monomer of Formula III is contacted with the disulphide of Formula II and free radical of the formula R^\bullet .

20. A process for preparing a copolymer of Formula I as claimed in claim 1 wherein
5 more than one monomer of Formula III is contacted with the disulphide of Formula II and free radical of the formula R^\bullet .
21. A process for preparing a block copolymer of Formula I as claimed in claim 1
10 wherein a first monomer of Formula III is contacted with the disulphide of Formula II and free radical of formula R^\bullet to produce a homopolymer of Formula I, said homopolymer being contacted with a second monomer of Formula III and a free radical of formula R^\bullet .
22. Use of a disulphide of Formula II to provide chain transfer in a free radical
15 polymerisation process.
23. Use of a disulphide of Formula II in the preparation of a chain transfer agent of Formula I for use in a free radical polymerisation process.
- 20 24. A process of claim 3 wherein the compound of Formula V is a thioacetal of benzoin.
25. A polymer prepared in accordance with any one of claims 1 to 23.
- 25 26. A process according to anyone of claims 1 to 3 wherein R^\bullet is capable of initiating free radical polymerisation.

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/AU 98/00569

A. CLASSIFICATION OF SUBJECT MATTER		
Int Cl ⁶ : C07C 327/36; C08F 2/38, 112/08, 120/14, 120/34, 212/08, 220/14, 220/34, 293/00		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) IPC Int Cl ⁶ C07C 327/36; C08F and keywords given below.		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) DERWENT (WPAT and JAPIO) keywords DITHIOESTER: and CHAIN TRANSFER CHEMICAL ABSTRACTS: REGISTRY NUMBER [5873-93-8]; keywords: chain transfer and disulfide.		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,A	WO, A1, 98/01478 (E.I. Du Pont De Nemours and Company) 15 January 1998 (see in particular scheme 3 on page 16).	21
A	WO, A1, 92/13902 (Commonwealth Scientific and Industrial Research Organisation) 20 August 1992 (see claim 1 and page 5 last paragraph)	1-26
A	EP, A2, 365792 (Bunawerke Hüls GmbH) 2 May 1990 (see entire document)	1-26
<input type="checkbox"/> Further documents are listed in the continuation of Box C <input checked="" type="checkbox"/> See patent family annex		
<p>* Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p>		
Date of the actual completion of the international search 1 September 1998		Date of mailing of the international search report 15 SEP 1998
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200 WODEN ACT 2606 AUSTRALIA Facsimile No.: (02) 6285 3929		Authorized officer NORMAN BLOM Telephone No.: (02) 6283 2238

INTERNATIONAL SEARCH REPORT **Information on patent family members**

International Application No.
PCT/AU 98/00569

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member					
EP, A2, 365792		AU, A1, 43887/89		BR, A, 89055500		DD, A5, 289546	
		DE, A1, 3836777		JP, A2, 2242802		US, A, 4965326	
		YU, A, 16672/89		ZA, A, 8908162			
WO, A1 92/13902		JP, A2, 4276098		US, A, 5342901		JP, A2, 4258603	
		JP, A2, 5271330					
WO, A1, 98/01478		AU, A1, 36033/97					
							END OF ANNEX